

AD

TECHNICAL REPORT ARCCB-TR-00002

**LEAD-TIN SOLDER CHARACTERIZATION BY
DIFFERENTIAL SCANNING CALORIMETRY**

MARK F. FLESZAR

JANUARY 2000



**US ARMY ARMAMENT RESEARCH,
DEVELOPMENT AND ENGINEERING CENTER
CLOSE COMBAT ARMAMENTS CENTER
BENÉT LABORATORIES
WATERVLIET, N.Y. 12189-4050**



APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

20000208 092

DISCLAIMER

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

The use of trade name(s) and/or manufacturer(s) does not constitute an official endorsement or approval.

DESTRUCTION NOTICE

For classified documents, follow the procedures in DoD 5200.22-M, Industrial Security Manual, Section II-19, or DoD 5200.1-R, Information Security Program Regulation, Chapter IX.

For unclassified, limited documents, destroy by any method that will prevent disclosure of contents or reconstruction of the document.

For unclassified, unlimited documents, destroy when the report is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE January 2000		3. REPORT TYPE AND DATES COVERED Final
4. TITLE AND SUBTITLE LEAD-TIN SOLDER CHARACTERIZATION BY DIFFERENTIAL SCANNING CALORIMETRY			5. FUNDING NUMBERS PRON No. 4EE2B069EH1A	
6. AUTHOR(S) Mark F. Fleszar				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army ARDEC Benet Laboratories, AMSTA-AR-CCB-O Watervliet, NY 12189-4050			8. PERFORMING ORGANIZATION REPORT NUMBER ARCCB-TR-00002	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army ARDEC Close Combat Armaments Center Picatinny Arsenal, NJ 07806-5000			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Presented at the 27 th North American Thermal Analysis Society Conference, Savannah, GA, 20-23 September 1999. Published in proceedings of the conference.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The electrolytic deposition of chromium on the bore of thick-walled, high-pressure cylinders uses a lead-tin alloy as the anode for the plating process. The anode is prepared by melting a lead-tin solder over a cylindrical copper core, which is then machined to the proper diameter. Using differential scanning calorimetry, the melting temperature of various ratios of lead-tin can be measured and a portion of the phase diagram can be established between the solid and liquid states. The melting temperature of a solder can then be measured and the composition can be obtained from the phase diagram.				
14. SUBJECT TERMS Thermal Analysis, Lead-Tin Alloy, Differential Scanning Calorimetry, Inductively Coupled Plasma Emission Spectroscopy			15. NUMBER OF PAGES 7	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED
				20. LIMITATION OF ABSTRACT UL

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION.....	1
EXPERIMENTAL PROCEDURE.....	1
RESULTS.....	2
CONCLUSION	5
BIBLIOGRAPHY	6

TABLES

1. DSC Results for Lead-Tin Binary Alloy	3
------------------------------------------------	---

LIST OF ILLUSTRATIONS

1. Lead-tine phase diagram.....	2
2. DSC scan for alloy 94.27 percent lead and 5.73 percent tin	3
3. Plot of onset of melting versus binary composition	4
4. Plot of enthalpy versus binary alloy composition	5

INTRODUCTION

A binary alloy of lead and tin is commonly used as an anode for the electrodeposition of chromium on a metal surface. The alloy used as the anode in the electrodeposition of hard chromium on a substrate should range between 90 and 95 weight percent lead, with the remainder tin. Emission spectroscopy is frequently used as an analytical method to verify the composition. To analyze samples by emission spectroscopy requires the acid digestion of solid samples with nitric acid, then the addition of a high concentration of hydrochloric acid to redissolve the tin. However, frequently all the tin will not go back into solution, depending on the weight percent of tin present. The ability to digest and keep both the lead and tin in solution makes the analysis very difficult. Occasionally the tin has to be precipitated, filtered, burned in a muffle oven, and weighed as an oxide. This is a very tedious and time-consuming process.

An alternate method of analysis utilizes differential scanning calorimetry (DSC) to melt the sample so the onset temperature and enthalpy of melting can be measured. Lead and tin form a binary alloy. From the phase diagram, as the lead composition decreases from 100 percent, the alloy melting temperature falls until it reaches the eutectic temperature. Thus, by measuring either the melting temperature or the melting enthalpy of the liquid + alpha transition to all liquid, one can determine the composition of the binary alloy. This method is faster and requires little sample preparation.

EXPERIMENTAL PROCEDURE

Samples were prepared using pure lead and tin. The samples used to prepare a calibration curve varied from 100 percent lead and no tin to 76.97 percent lead and 23.03 percent tin. The lead used to prepare the standard calibration curve was reagent grade lead sticks from Matheson, Coleman and Bell. The tin was purchased from Perkin-Elmer Corporation's catalogue of DSC reference materials and was certified as 99.99 percent pure.

To prepare the various calibration samples, the lead sticks were cut into thin slaps using a razor blade to expose two fresh surfaces free of oxide. A rectangular segment of the slab was cut from the center to ensure that no oxide was present, then the specimen was weighed. A section of the tin reference material was cut using a separate razor blade (oxide formation was not a problem with the tin), weighed, and then placed on top of the flat lead section in an aluminum pan. The open pan was placed in a Perkin-Elmer DSC-7 in the sample cell and an open blank aluminum pan placed in the reference cell. The DSC was allowed to purge with nitrogen for 10 minutes prior to rapidly heating the sample to 400°C. The sample was held at temperature for 10 minutes, then rapidly cooled to 50°C. It was then heated at a rate of 10°C/minute from 50°C to 350°C. The heat flow versus temperature was recorded.

Each calibration sample and anode sample was analyzed in triplicate. The onset temperature of melting, peak temperature, and enthalpy of melting were measured and recorded for the alpha + liquid to liquid transition for the binary alloy.

RESULTS

Figure 1 shows the binary alloy phase diagram for lead-tin with the melting temperature for the alloy varying between 327°C for pure lead and 232°C for pure tin. At the eutectic point of 62 percent tin and 38 percent lead, there is a melting temperature of 183°C compared to the melting temperature for pure lead, 327°C. As we move along the phase boundary between the alpha + liquid and liquid line, the melting temperature increases with increasing lead concentration. In the range of interest, 85 percent lead and 15 percent tin to pure lead, the alpha solid partially melts going to liquid + alpha. On further heating, the remaining alpha solid melts.

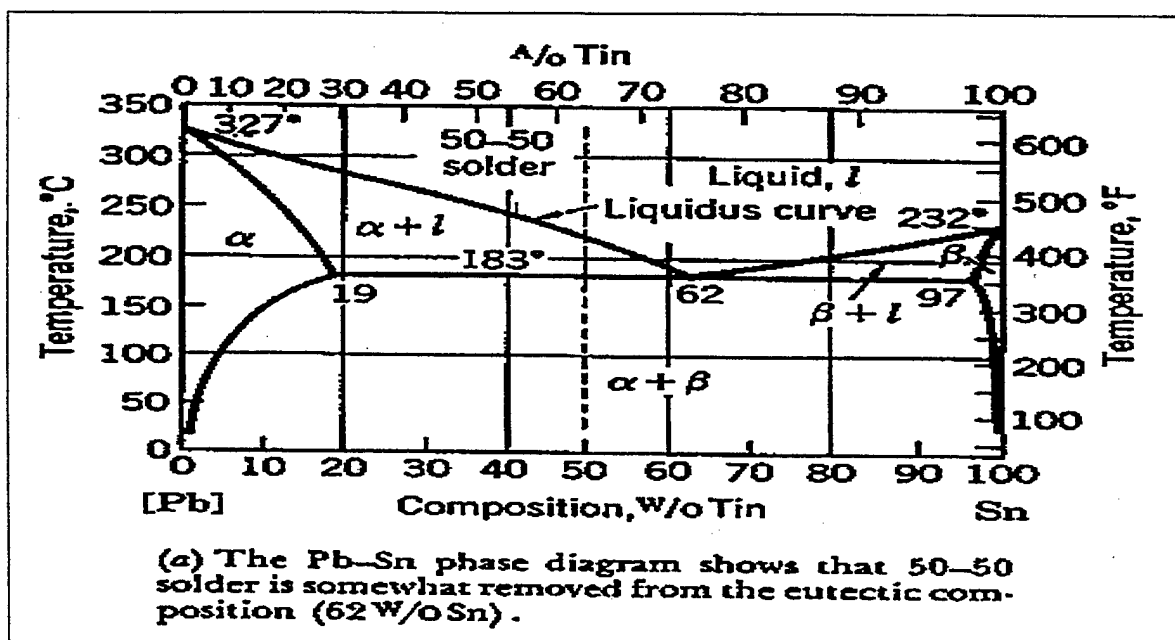


Figure 1. Lead-tin phase diagram.

Figure 2 is a typical DSC scan for the binary melting of lead-tin. The phase diagram shows that as the temperature increases, below 19 percent tin, the alpha + beta solid goes to all alpha solid. Above 19 percent tin, the alpha + beta solid goes to alpha + liquid. As the temperature continues to increase, below 19 percent tin, some of the alpha solid melts. Eventually, the remaining alpha solid goes to liquid. Examining the melting peak, a shoulder can be seen on the left side of the peak revealing the overlapping of two peaks. The first peak or shoulder shows partial melting of the alpha solid, and the second peak shows melting of the remaining alpha solid. Thus, the area under the melting peak is a composite of the enthalpy for the partial melting of the alpha solid going to alpha + liquid and the complete melting of the remaining alpha in the alpha + liquid region.

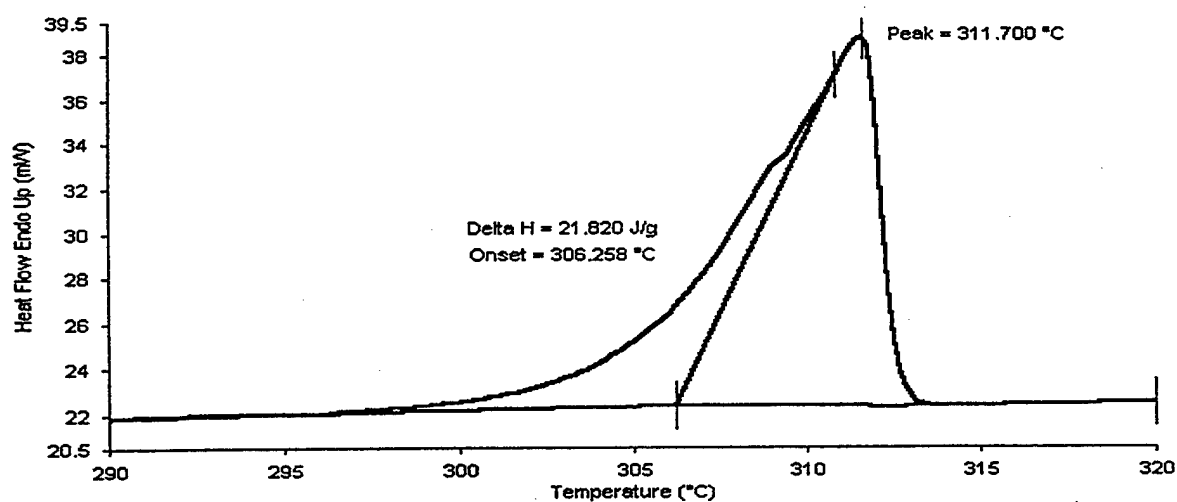


Figure 2. DSC scan for alloy 94.27 percent lead and 5.73 percent tin.

Table 1 lists the binary alloy composition, onset of melting temperature, melting enthalpy, and peak melting temperature for a series of high purity lead-tin alloys. Comparing the temperatures along the liquidus curve in the phase diagram with the onset of melting temperature in the table, it can be seen that the values in the table fall below the liquidus curve, while the peak temperatures show good agreement with the liquidus curve. This is probably due to the inability of the DSC to resolve the alpha to alpha + liquid transition from the alpha + liquid to all-liquid transition.

Table 1. DSC Results for Lead-Tin Binary Alloy

Pb (%)	Sn (%)	Weight (mg)	Onset Temp (°C)	Enthalpy (J/g)	Peak Temp (°C)
100.00	0.00	20.38	325.87	23.07	328.41
97.17	2.86	24.83	316.70	22.60	319.81
96.89	3.11	23.08	316.48	22.69	320.81
94.80	5.20	18.79	308.35	21.61	313.48
94.27	5.73	21.30	305.39	21.92	311.81
92.66	7.34	24.80	302.37	22.63	308.57
91.96	8.04	23.13	297.84	21.23	304.48
89.98	10.02	19.96	289.95	21.03	299.92
89.05	10.95	24.84	286.23	20.37	296.97
82.04	17.96	24.33	260.49	16.29	278.81
76.97	23.03	25.71	258.49	16.10	279.03

Figure 3 plots the onset of melting for the alpha + liquid transition to all liquid versus the weight percent of lead in the samples. As the percentage of tin increases, the melting temperature of the binary alloy decreases. Over the range of zero to 23.03 percent tin, the onset melting temperature decreased by 67.38°C. A sample of a typical lead-tin solder used to prepare a plating anode was analyzed using the calibration curve plotted in Figure 3. The sample had a melting onset temperature of 303.0°C and an enthalpy of 22.09 J/g. From the calibration curve, a melting temperature of 303.0°C corresponds to a composition of 93.5 percent lead and 6.5 percent tin.

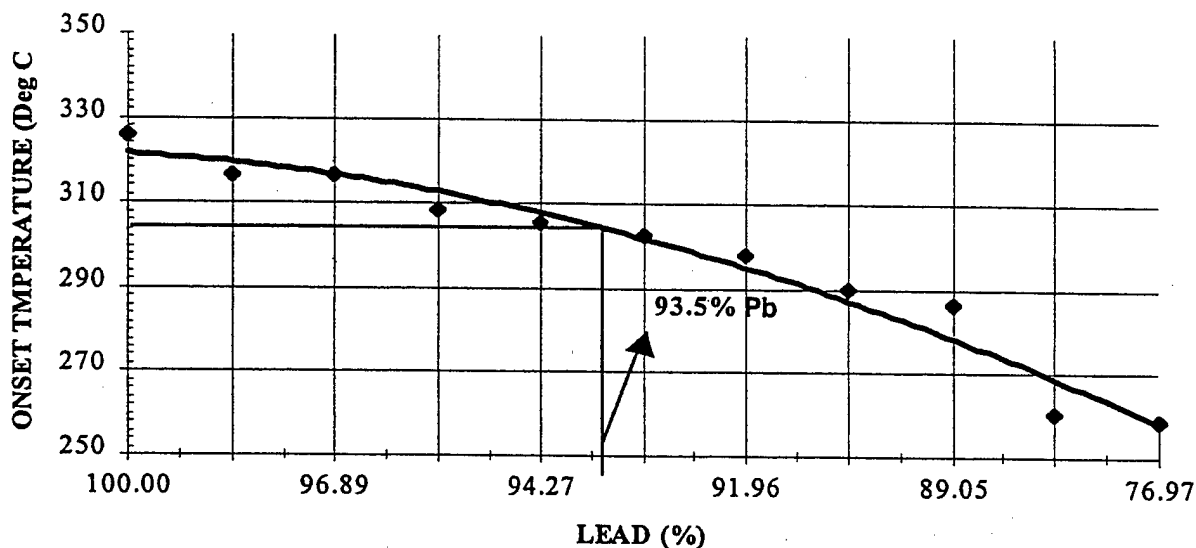


Figure 3. Plot of onset of melting versus binary composition.

Figure 4 plots the enthalpy of melting versus the weight percent of lead in the samples. In the range of 92.5 to 100 percent lead, the rate of change or slope of the curve is small, resulting in a small change in the melting enthalpy over a large portion of the curve in the region of interest. A change of less than 2 J/g was observed, while the lead concentration varied by 7.5 percent. Thus, the sensitivity to small changes in the lead-tin concentration in this range is difficult to detect. Looking at the calibration curve in Figure 4, the lead-tin composition for the anode sample was calculated to be 94.3 percent lead and 5.7 percent tin. This is a significant difference from the 93.5 percent lead and 6.5 percent tin concentration obtained for the melting point data. As a matter of fact, with a standard deviation of ± 0.22 J/g in the sample, the lead concentration can vary from approximately 93 to 95 percent lead.

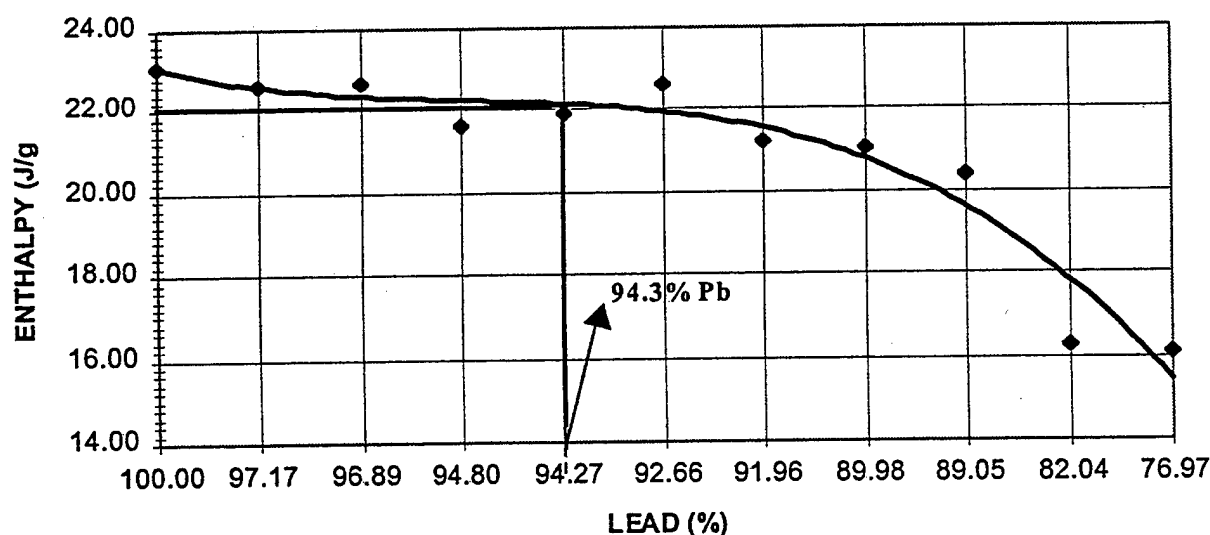


Figure 4. Plot of enthalpy versus binary alloy composition.

CONCLUSION

Differential scanning calorimetry provides an alternative method of analysis for the determination of a binary alloy composition of lead-tin. Compared to inductively coupled plasma emission spectroscopy, it provides a faster method of analysis with very little sample preparation. The use of onset melting temperature appears to be more accurate than melting enthalpy to determine the lead-tin composition in the region of zero to 7.0 percent tin, due to the small change observed in the melting enthalpy over that portion of the curve. However, caution should be used when applying the onset melting temperature method to ensure that the alloy does not contain any other alloying elements that could affect the sample melting temperature and enthalpy.

BIBLIOGRAPHY

1. Guy, A.G., *Essentials of Material Science*, McGraw-Hill Book Company, New York, 1976, pp. 66-67.
2. Wendlandt, W.W., *Thermal Analysis*, 3rd Edition, John Wiley and Sons, New York, 1986.
3. Turi, A.A., *Thermal Characterization of Polymeric Materials*, Academic Press, Inc., Orlando, 1981.
4. Higgins, R.A., *Engineering Metallurgy, Part 1: Applied Physical Metallurgy*, Edward Arnold, A Division of Hodder and Stoughton, London, 1993, pp. 196-200.
5. Ralls, K.M., Courtney, T.H., and Wulff, J., *Introduction to Materials Science and Engineering*, John Wiley and Sons, New York, 1976, pp. 233-234.

TECHNICAL REPORT INTERNAL DISTRIBUTION LIST

	<u>NO. OF COPIES</u>
TECHNICAL LIBRARY ATTN: AMSTA-AR-CCB-O	5
TECHNICAL PUBLICATIONS & EDITING SECTION ATTN: AMSTA-AR-CCB-O	3
OPERATIONS DIRECTORATE ATTN: SIOWV-ODP-P	1
DIRECTOR, PROCUREMENT & CONTRACTING DIRECTORATE ATTN: SIOWV-PP	1
DIRECTOR, PRODUCT ASSURANCE & TEST DIRECTORATE ATTN: SIOWV-QA	1

NOTE: PLEASE NOTIFY DIRECTOR, BENÉT LABORATORIES, ATTN: AMSTA-AR-CCB-O OF ADDRESS CHANGES.

TECHNICAL REPORT EXTERNAL DISTRIBUTION LIST

	<u>NO. OF COPIES</u>		<u>NO. OF COPIES</u>
DEFENSE TECHNICAL INFO CENTER ATTN: DTIC-OCA (ACQUISITIONS) 8725 JOHN J. KINGMAN ROAD STE 0944 FT. BELVOIR, VA 22060-6218	2	COMMANDER ROCK ISLAND ARSENAL ATTN: SIORI-SEM-L ROCK ISLAND, IL 61299-5001	1
COMMANDER U.S. ARMY ARDEC ATTN: AMSTA-AR-WEE, BLDG. 3022 AMSTA-AR-AET-O, BLDG. 183 AMSTA-AR-FSA, BLDG. 61 AMSTA-AR-FSX AMSTA-AR-FSA-M, BLDG. 61 SO AMSTA-AR-WEL-TL, BLDG. 59 PICATINNY ARSENAL, NJ 07806-5000	1 1 1 1 1 2	COMMANDER U.S. ARMY TANK-AUTMV R&D COMMAND ATTN: AMSTA-DDL (TECH LIBRARY) WARREN, MI 48397-5000	1
DIRECTOR U.S. ARMY RESEARCH LABORATORY ATTN: AMSRL-DD-T, BLDG. 305 ABERDEEN PROVING GROUND, MD 21005-5066	1	U.S. ARMY AVIATION AND MISSILE COM REDSTONE SCIENTIFIC INFO CENTER ATTN: AMSAM-RD-OB-R (DOCUMENTS) REDSTONE ARSENAL, AL 35898-5000	2
DIRECTOR U.S. ARMY RESEARCH LABORATORY ATTN: AMSRL-WM-MB (DR. B. BURNS) ABERDEEN PROVING GROUND, MD 21005-5066	1	COMMANDER U.S. ARMY FOREIGN SCI & TECH CENTER ATTN: DRXST-SD 220 7TH STREET, N.E. CHARLOTTESVILLE, VA 22901	1
COMMANDER U.S. ARMY RESEARCH OFFICE ATTN: TECHNICAL LIBRARIAN P.O. BOX 12211 4300 S. MIAMI BOULEVARD RESEARCH TRIANGLE PARK, NC 27709-2211	1		

NOTE: PLEASE NOTIFY COMMANDER, ARMAMENT RESEARCH, DEVELOPMENT, AND ENGINEERING CENTER,
BENET LABORATORIES, CCAC, U.S. ARMY TANK-AUTOMOTIVE AND ARMAMENTS COMMAND,
AMSTA-AR-CCB-O, WATERVLIET, NY 12189-4050 OF ADDRESS CHANGES.
